

Capture-zone distribution in one-dimensional sub-monolayer film growth: a fragmentation theory approach

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Abstract.

The distribution of capture zones formed during the nucleation and growth of point islands on a one-dimensional substrate during monomer deposition is considered for general critical island size i . A fragmentation theory approach yields the small and (for $i = 0$) large size asymptotics for the capture zone distribution (CZD) under the assumption of no neighbour-neighbour gap size correlation. These CZD asymptotic forms are different to those of the Generalised Wigner Surmise which has recently been proposed for island nucleation and growth models, and we discuss the reasons for the discrepancies.

AMS classification scheme numbers: 45J05; 45M05; 78M35

1. Introduction

Island nucleation and growth during the early stages of thin film deposition has attracted much attention over the last few decades [28, 8, 17]. The islands that arise from the aggregation of the deposited material form the building blocks for nanostructure growth [24, 12] and subsequent film morphology [16], and so are of direct technological interest. The growth process is amenable to Monte Carlo (MC) simulation, which in turn have inspired many theoretical analyses which revisit meanfield rate equations (for example see references

[5, 2, 23]). The most striking aspect to arise from these models has been the identification of scale invariance in the growth process, exemplified in the island size distribution (ISD) [1]. It has been recognised that in order to understand the ISD, one cannot simply rely on mean field equations since they do not always yield the correct form for it [6] and in some cases do not even display the fundamental scaling property seen in simulation and experiment [3, 26].

In order to better understand the ISD, we must consider the growth rate of an island that has nucleated on the substrate. It grows by capturing deposited monomers, which diffuse to it across the substrate. The growth rate of the island is therefore dependent on its capture zone, defined as the region of substrate closer to this island than to any other [18, 19, 11]; monomers deposited into the island's capture zone are more likely to diffuse to it than to any other competing island. This concept has been successfully used for the ISD found in growth on both two- [18, 6] and one-dimensional substrates [7]. The latter model is of particular interest, since it can be analysed in great detail, and it is the subject of the current paper.

Recently there has been renewed interest in the capture zones and associated size distribution (CZD) where it has been proposed that the CZD follows the Generalised Wigner Surmise [21, 22]. In particular, it has been suggested [21] that the CZD obeys

$$P(s) = a_\beta s^\beta \exp(-b_\beta s^2), \quad (1)$$

where

$$a_\beta = \frac{2\Gamma\left(\frac{\beta+2}{2}\right)^{\beta+1}}{\Gamma\left(\frac{\beta+1}{2}\right)^{\beta+2}}, \quad b_\beta = \left[\frac{\Gamma\left(\frac{\beta+2}{2}\right)}{\Gamma\left(\frac{\beta+1}{2}\right)} \right]^2$$

are normalisation constants so that

$$\int_0^\infty P(s) ds = \int_0^\infty sP(s) ds = 1,$$

and

$$\beta = \begin{cases} \frac{2}{d}(i+1) & \text{if } d=1,2 \\ (i+1) & \text{if } d=3. \end{cases} \quad (2)$$

Here $s = x/\langle x \rangle$ is the capture zone size x scaled to its average $\langle x \rangle$ at any time t in the aggregation regime [2]. The aggregation regime is such that the island density is greater than the monomer density, so that further nucleation is a slow process compared to the island growth due to monomer capture.

Despite the excellent visual comparisons between equation (1) and MC data taken from the literature [21], the validity of the GWS has already been challenged. Shi et al. [25] studied

$i = 1$ point island models in $d = 1, 2, 3, 4$ dimensions, finding that the CZD is more sharply peaked than the GWS suggests for $d = 1, 4$ and a better choice of $\beta = 3$ rather than $\beta = 2$ for $d = 2, 3$. Li et al. [14] also question the $i = 1, d = 2$ GWS form for the CZD, proposing their own form based on a sophisticated theory for capture zone evolution in two dimensions [11].

We also note that there is a conflict in the small and large size form of (1) and that of the theory presented in [7] for the one-dimensional (1-D) nucleation and growth of point islands. The work in [7] focused on the case with critical island size $i = 1$, where we impose the condition that $i + 1$ monomers must coincide in order to nucleate a stable, immobile island. The analysis in [7] utilises a fragmentation theory approach (as described below) which we consider to be physically reasonable. It is therefore of interest to ask whether a similar conflict exists for other critical island sizes. In this work we extend the 1-D point-island fragmentation approach to $i = 0, 1, 2, 3, \dots$ and show that the small-size conflict with [21] holds for all non-negative integers i . The case of $i = 1$ in this model has recently been considered in [13], where the form of equation (1) has been extended in light of MC simulation data. Here we retain a focus on the comparison between the original GWS of equation (1) and the fragmentation model for general i .

In [7] a MC simulation was presented, where monomers are randomly deposited at rate F onto a line of points which represents the substrate. The monomers diffuse (with diffusion constant D) by nearest neighbour hops until they nucleate a new island, or are adsorbed by hopping onto an existing island. Since nucleation is a rare event in the aggregation regime, it is assumed [7] that the average monomer density $n_1(x)$ in the gap (length y) between two neighbouring islands obeys its saturated form

$$n_1(x) = Rx(y - x), \quad 0 < x < y, \quad (3)$$

where we have set $R = \frac{F}{2D}$.

Furthermore, this density profile is then used to predict the probability of a nucleation occurring at position x in the gap, which we take to be proportional to $n_1^{i+1}(x)$. In adopting this form, it is assumed that the nucleation arises from the congregation of $(i + 1)$ “mature” monomers that have explored their gap and lost memory of their deposition events.

In this work we will adopt the same approach as in [7] and derive a gap-size evolution equation for $i = 0, 1, 2, \dots$. From this equation, we obtain information on similarity solutions which involve a reduced gap size distribution function $\phi(y)$. We are then able to construct the CZD under the assumption used in [7] that due to the stochastic nature of the nucleation process there are no neighbour-neighbour gap size correlations in the system. Under this

assumption, we can write

$$P(s) = 2 \int_0^{2s} \phi(y) \phi(2s - y) dy. \quad (4)$$

We shall then show that the small size form for $P(s)$ given by equation (4) is different to that of equation (1). In particular, the small size power dependence from equation (4) will prove to be an odd power of s , whereas equation (1) always gives an even power for one-dimensional substrate. We also prove that the large-size forms in equations (1) and (4) for the spontaneous nucleation model ($i = 0$) are in similar disagreement.

2. The gap evolution equation

We model the one-dimensional aggregation regime by regarding nucleated islands as points on a line. Our aim is to obtain an equation that describes the evolution of the gaps between adjacent islands. Let $n(x, t)$ denote the number concentration of gaps of width x at time t . Since any new nucleation event that occurs in a ‘parent’ gap of width y will result in the creation of two ‘daughter’ gaps of widths x and $y - x$, it is clear that the evolution of the system of gap sizes can be interpreted as a fragmentation process. Processes of this type are usually modelled by the linear fragmentation equation

$$\frac{\partial}{\partial t} n(x, t) = -a(x)n(x, t) + \int_x^\infty b(x|y)a(y)n(y, t) dy. \quad (5)$$

In the case of gap sizes, $a(x)$ represents the rate at which gaps of width x fragment (due to nucleation) and $b(x|y)$ describes the distribution of gaps of width x resulting from the fragmentation of a parent gap of width $y > x$. Since each new nucleation leads to the birth of only two daughter gaps, and since the total length of all the gaps is preserved, we require b to satisfy

$$\int_0^y b(x|y) dx = 2 \quad \text{and} \quad \int_0^y xb(x|y) dx = y. \quad (6)$$

To obtain appropriate functions a and b , as explained above, we follow the approach used by Blackman and Mulheran [7]. Therefore, we assume that, in the aggregation regime, the density of monomers in a gap of width y is given by (3).

By the reasoning given in the Introduction, the probability of a new nucleation occurring in a gap of width y may be taken as being proportional to

$$a(y) = R^{i+1} \int_0^y x^{i+1}(y-x)^{i+1} dx = R^{i+1} B(i+2, i+2) y^{2i+3}, \quad (7)$$

where $B(\cdot, \cdot)$ denotes the Beta function. Then, given that a nucleation event has caused a gap of width y to fragment, with fragmentation rate $a(y)$, the probability that it will occur at a scaled position $r = x/y$ in $[r_0, r_0 + dr] \subseteq [0, 1]$ is given by $h(r)dr$, where

$$h(r) = R^{i+1}r^{i+1}(1-r)^{i+1}, \quad 0 \leq r \leq 1. \quad (8)$$

Since $x \in [x_0, x_0 + dx] \Leftrightarrow x/y \in [x_0/y, x_0/y + dx/y] \Leftrightarrow r \in [r_0, r_0 + dr]$, the probability that the nucleation occurs at $x \in [x_0, x_0 + dx]$ is given by $h(x_0/y)dx/y$. Therefore, we take

$$b(x|y) = k h(x/y)/y, \quad (9)$$

where

$$k = \frac{1}{R^{i+1}B(i+3, i+2)}$$

so that (6) is satisfied. This leads to

$$b(x|y) = y^{-2i-3}x^{i+1}(y-x)^{i+1}/B(i+3, i+2),$$

and equation (5) therefore becomes

$$\begin{aligned} \frac{\partial}{\partial t} n(x, t) = & R^{i+1} \left(-B(i+2, i+2) x^{2i+3} n(x, t) \right. \\ & \left. + 2 \int_x^\infty x^{i+1}(y-x)^{i+1} n(y, t) dy \right). \end{aligned} \quad (10)$$

A simple re-scaling of the time variable then yields the gap-size evolution equation

$$\frac{\partial}{\partial t} n(x, t) = -B(i+2, i+2) x^{2i+3} n(x, t) + 2 \int_x^\infty x^{i+1}(y-x)^{i+1} n(y, t) dy. \quad (11)$$

This equation is a particular case of the linear, homogeneous fragmentation equation

$$\frac{\partial}{\partial t} n(x, t) = -c_\sigma x^\sigma n(x, t) + c_\sigma \int_x^\infty y^{\sigma-1} K(x/y) n(y, t) dy \quad (12)$$

for some $\sigma \geq 0$ in which $K(x/y)$, a homogeneous function of degree zero, determines the number of daughter “particles” of size x obtained when a parent “particle” of size $y > x$ fragments. There is a considerable literature on equations of this type, and various mathematical techniques have been used in the analysis of (12). For example, the theory of strongly continuous semigroups of operators can be applied to establish the existence and uniqueness of physically meaningful solutions; see, for example, [4, Chapter 8]. Similarity solutions have also been investigated by a number of authors, including Ziff and McGrady

[30] (for the case $i = 0$ in equation (11)), Cheng and Redner [9] and Treat [27]. As shown in [27], similarity solutions can be written in the form

$$n^*(x, t) = \frac{N^{*2}(t)}{V} \phi\left(\frac{N^*(t)x}{V}\right) \quad (13)$$

where the *reduced distribution* ϕ is required to satisfy an integral equation and is normalised so that

$$\int_0^\infty \phi(y) dy = \int_0^\infty y\phi(y) dy = 1,$$

and

$$N^*(t) := \int_0^\infty n^*(x, t) dx, \quad V := \int_0^\infty xn^*(x, t) dx,$$

are, respectively, the zeroth and first moments of n^* . An explicit expression, involving the Meijer G -function, is derived in [27, Section 6] for the specific case when the *daughter distribution* function K in equation (12) takes the form

$$K(r) = r^\gamma(b_0 + b_1r + \cdots + b_pr^p), \quad (14)$$

p is a non-negative integer, $b_0, \dots, b_p \in \mathbb{R}$, and $0 \leq r \leq 1$. We shall make use of the simple case $p = 1$, discussed in [27, Section 7.2], in the next section.

Asymptotic properties of the function ϕ have also been established for more general homogeneous functions K . In particular, in [9] and [27, Section 5], it is shown that

$$\phi(y) = \mathcal{O}(y^\gamma) \text{ as } y \rightarrow 0, \quad (15)$$

provided that $\lim_{r \rightarrow 0} r^{-\gamma-2} \int_0^r sK(s)ds$ exists and is non-zero, and

$$\phi(y) = \mathcal{O}y^{K(1)-2} \exp(-cy^\sigma) \text{ as } y \rightarrow \infty, \quad (16)$$

for some constant $c > 0$.

The questions of existence and stability, in an appropriately defined sense, of similarity solutions to fragmentation equations of homogeneous type have also been addressed in [10].

In the case of the gap fragmentation equation (11), (15) and (16) lead directly to the following result.

Theorem 1. *The equation (11) has a similarity solution of the form (13) where the gap size distribution ϕ satisfies*

- I. $\phi(y) = \mathcal{O}(y^{i+1})$ as $y \rightarrow 0$;
- II. $\phi(y) = \mathcal{O}(y^{-2} \exp(-cy^{2i+3}))$ as $y \rightarrow \infty$ for some $c > 0$.

The task now is to understand, given the information we have for $\phi(y)$, the behaviour of the convolution (4). The situation for small s is straightforward for any i , but for large s we only have a result if $i = 0$. The derivation of the asymptotics is non-trivial and requires the use of a multi-dimensional version of Laplace's method. This is the content of the next two sections.

3. CZD asymptotics

The small s behaviour of $P(s)$ for arbitrary i can be obtained immediately from part I of Theorem 1 and equation (4):

Theorem 2. *For the critical island size $i \geq 0$, we have*

$$P(s) = \mathcal{O}(s^{2i+3}) \text{ as } s \rightarrow 0,$$

where $P(s)$ is the 1-D CZD.

Proof. We have, for small s and $0 < y < 2s$,

$$\phi(y) = \mathcal{O}(y^{i+1}), \quad \phi(2s - y) = \mathcal{O}((2s - y)^{i+1}),$$

Hence $\phi(y)\phi(2s - y) = \mathcal{O}(s^{i+1}y^{i+1})$ and therefore

$$P(s) = 2 \int_0^{2s} \phi(y)\phi(2s - y) dy = \mathcal{O}(s^{i+1}s^{i+2}) = \mathcal{O}(s^{2i+3})$$

as $s \rightarrow 0$. □

By Theorem 2, the exponent is always odd which differs from the GWS prediction that we should have $P(s) = \mathcal{O}(s^\beta)$ where $\beta = 2(i + 1)$ is always even when $d = 1$. Hence we are led to the conclusion that the GWS does not describe the behaviour of the scaling function $P(s)$ as $s \rightarrow 0$ for any $i \geq 0$ if we accept that the gap evolution equation (11), and the relation between $\phi(y)$ and the capture zone distribution $P(s)$ given by (4), are correct.

The next aim is to understand the asymptotic behaviour of $P(s)$ in (4) for large s . For this, it would appear that an explicit and reasonably simple, formula for the reduced distribution $\phi(y)$ is required. In the case $i = 0$, the gap fragmentation equation (11) becomes

$$\frac{\partial}{\partial t} n(x, t) = -\frac{x^3}{6} n(x, t) + 2 \int_x^\infty x(y - x) n(y, t) dy,$$

which is the equation analysed by Ziff and McGrady in [30]. Note also, that in this case the homogeneous function K can be obtained from the general *linear daughter distribution*,

$$K(r) = r^\gamma(b_0 + b_1 r), \quad (17)$$

investigated by Treat in [27, Section 7.2], by setting $\gamma = 1, b_0 = 12, b_1 = -12$. On applying [27, (7.6)], we deduce that $\phi(y) = \bar{\phi}(\eta)$, where $\eta = y^3/\mu^3$,

$$\mu = \frac{\Gamma(2/3)\Gamma(7/3)}{\Gamma(4/3)\Gamma(2)} = \frac{4}{3}\Gamma(2/3)$$

and

$$\begin{aligned} \bar{\phi}(\eta) &= \frac{A}{\mu} \eta^{1/3} e^{-\eta} \frac{1}{\Gamma(1)} \int_0^\infty (1+s)^{-4/3} \exp(-s\eta) ds, \quad A = 3/\Gamma(2/3), \\ &= \frac{A}{\mu} \eta^{1/3} \int_1^\infty z^{-4/3} \exp(-z\eta) dz = \frac{A}{\mu} \eta^{2/3} \int_\eta^\infty u^{-4/3} \exp(-u) du. \end{aligned}$$

Hence

$$\phi(y) = \frac{A}{\mu^3} y^2 \int_{y^3/\mu^3}^\infty u^{-4/3} \exp(-u) du \quad (18)$$

$$= \frac{3y}{\Gamma(\frac{2}{3})\mu^2} \int_1^\infty v^{-4/3} e^{-v(y/\mu)^3} dv. \quad (19)$$

Note that Ziff and McGrady proposed a similar formula for ϕ but with the constant $\mu^3 (\approx 5.88)$ in the lower limit of integration in (18) replaced by 6. That the correct choice is μ^3 follows from the fact that this leads to

$$\int_0^\infty \phi(y) dy = \int_0^\infty y \phi(y) dy = 1.$$

This explicit representation of $\phi(y)$ for the case $i = 0$ enables us to obtain the following result.

Theorem 3. *If $i = 0$ then*

$$P(s) = \mathcal{O} \left(s^{-9/2} \exp \left(-2 \frac{s^3}{\mu^3} \right) \right) \text{ as } s \rightarrow \infty.$$

The next section is devoted to proving this theorem.

4. Proof of Theorem 3

The arguments of Wong [29, Ch. VIII, Sections 8 and 11] allow us to obtain the following general theorem about two-dimensional Laplace integrals.

Let

$$J(\lambda) = \iint_D g(v, w) e^{-\lambda f(v, w)} dv dw, \quad (20)$$

where λ is a large parameter, $D \subset \mathbb{R}^2$, and let $f(v, w)$, $g(v, w)$ be smooth functions on D .

We have

Theorem 4. *If (v_0, w_0) is the global minimum of $f(v, w)$ on \overline{D} and is a critical point of the third kind, then as $\lambda \rightarrow \infty$, $J(\lambda) = \mathcal{O}(\lambda^{-2} e^{-\lambda f(v_0, w_0)})$.*

We remind the reader that (v_0, w_0) is a **critical point of the third kind** of $f(v, w)$ if it is an extremum point of f on D belonging to the boundary of D through which pass two intersecting tangent lines, neither of which coincides with the tangent to the level curve $\psi(v, w) = \psi(v_0, w_0)$ at (v_0, w_0) .

Our aim is to understand the asymptotics of (4) as $s \rightarrow \infty$ in the case of $i = 0$ using the explicit form (19).

If we let $u = y^3 v / \mu^3$ in (18), substitute the resulting expression for $\phi(y)$ into (4) and then put $y = 2sz$, we have

$$P(s) = \frac{144s^3}{\mu^4 \Gamma(2/3)^2} \int_1^\infty \int_1^\infty (vw)^{-4/3} \int_0^1 z(1-z) e^{-(2s)^3(z^3 v + (1-z)^3 w)/\mu^3} dz dv dw. \quad (21)$$

Our strategy is to use Laplace's method to evaluate the inner integral, which will give us a two-dimensional Laplace integral on $D = (1, \infty) \times (1, \infty)$, which will be attacked using Theorem 4.

For any $(v, w) \in D$, set $S(z) = z^3 v + (1-z)^3 w$. If $v = w$, $S(z)$ has a unique minimum at $z_+ = 1/2$. If $v \neq w$, critical points of $S(z)$ satisfy $(v-w)z^2 + 2wz - w = 0$, so that

$$z_\pm = \frac{-w \pm \sqrt{vw}}{v-w}.$$

It is easy to check that $S''(z_+) = 6\sqrt{vw} > 0$, so that the minimum of $S(z)$ is obtained at

$$z_+ = \frac{-w + \sqrt{vw}}{v-w} = \frac{\sqrt{w}}{\sqrt{w} + \sqrt{v}} \in (0, 1). \quad (22)$$

Hence by Laplace's formula, setting $\lambda = \frac{8s^3}{\mu^3}$, we have, as $\lambda \rightarrow \infty$,

$$I_1(\lambda) := \int_0^1 z(1-z) \exp(-\lambda S(z)) dz \sim z_+(1-z_+) e^{-\lambda S(z_+)} \sqrt{\frac{2\pi}{\lambda S''(z_+)}}.$$

Note that

$$S(z_+) = \frac{wv}{(\sqrt{w} + \sqrt{v})^2},$$

which reaches its minimum value $1/4$ on D at the corner point $(1, 1)$.

Thus, the inner integral in (21) satisfies, as $s \rightarrow \infty$,

$$I_1\left(\frac{8s^3}{\mu^3}\right) \sim \left(\frac{8s^3}{\mu^3}\right)^{-1/2} \rho(v, w) \exp\left(-\frac{8s^3}{\mu^3} \frac{wv}{(\sqrt{w} + \sqrt{v})^2}\right),$$

where we have put

$$\rho(v, w) = \sqrt{\frac{2\pi}{S''(z_+)}} z_+(1-z_+).$$

This means by (21) that

$$P(s) = \mathcal{O}\left(s^{3/2} \int_1^\infty \int_1^\infty \rho(v, w) (vw)^{-4/3} \exp\left(-\frac{8s^3}{\mu^3} \frac{wv}{(\sqrt{w} + \sqrt{v})^2}\right) dv dw\right), \quad (23)$$

and now invoking Theorem 4 we have, as $s \rightarrow \infty$,

$$P(s) = \mathcal{O}\left(s^{3/2} e^{-(8s^3/\mu^3)(1/4)} \left(\frac{8s^3}{\mu^3}\right)^{-2}\right),$$

i.e. $P(s) = \mathcal{O}\left(s^{-9/2} e^{-2s^3/\mu^3}\right)$ as required.

5. Conclusions

In this paper we have shown that the Blackman and Mulheran model [7] for the nucleation and growth of point islands on a one-dimensional (1-D) substrate, based on a fragmentation equation approach, yields a capture zone distribution (CZD) that is different to the Generalised Wigner Surmise (GWS) in equation (1) [21]. The asymptotics of the CZD

are measurable in MC simulation, allowing these theories to be tested, and we will present our analyses of simulations elsewhere [20]. Here we will conclude this current work with a discussion of how the two theoretical approaches differ and how they might be reconciled.

It is interesting to note that the justification for the relationship between the parameter β in equation (1) and the critical island size, as given in equation (2), is based on the same physical model analysed in this paper. In [21], the island nucleation rate is discussed in terms of the monomer density n , and the probability of $(i + 1)$ monomers coinciding is used to give the nucleation rate as $\sim n^{i+1}$. This of course is exactly the physical basis we have used, so it is worthwhile considering why [21] end up with different power-law behaviour for small capture zone sizes.

Let us summarise the phenomenological arguments used in [21]. Firstly the authors consider the nucleation rate within capture zones with size s , which have a relative density $P(s)$, using the mean field value of the monomer density n . They then reconsider the nucleation rate within a small zone of size s using the locally averaged monomer density. In one space dimension, they argue that this density $\sim ns^2$. Equating the two rates, $P(s)n^{i+1} \sim (ns^2)^{i+1}$ yields their law for β in 1-D nucleation so that $P(s) \sim s^{2i+2}$ for small s . We note that recently the originators of equation (1) have considered alternative forms to the Gaussian tail following evidence from their own MC simulations with $i = 1$.

From our perspective, we see a number of problems with this argument. Firstly, the method of constructing the two alternative nucleation rates appears internally inconsistent, using both the mean field monomer density n and a local approximation. Usually this approach would involve taking averages of the latter to reach consistency with the former [3, 7], however this was not done in [21]. The second criticism, more pertinent to this paper, is that the nucleation rate using the locally averaged monomer density within a capture zone has not been justified. Indeed, in [22], the authors revise their argument for two dimensional substrates and use a spatially dependent monomer density $n(r)$ within a capture zone to derive the nucleation rate for the zone. This involves integrating $n^{i+1}(r)$ over the zone, reminiscent of the approach used elsewhere for the two dimensional substrate [15], resulting in a different relationship $\beta(i)$ which better fits Monte Carlo data.‡

Presumably, this type of modification can be taken forward to the 1-D case discussed here. Following the same line of argument, we might take the local monomer density in a small capture zone size s as that from two gaps of size $s/2$, using the form of equation (3) above. If we do this, we will end up with the formula $\beta(i) = 2i + 3$, thereby agreeing with the small-size

‡ In [22], the authors use $n(r) \sim R^2 - r^2$, $R_i < r < R$, with R_i and R being the island and circular capture zone radii. It is not clear what motivated the choice of boundary conditions for this form; we would have expected the monomer density to be zero at the island edge, rising to a maximum at the capture zone radius so that its gradient is zero at this boundary [15].

CZD behaviour we have derived in this work. Although this does go some way to reconciling the two approaches, we consider that this line of reasoning is heuristic at best, and much prefer the more rigorous methods adopted in our work presented here in this paper.

The second component of the GWS in equation (1) is the large-size behaviour of the CZD. Here too we see a conflict with the fragmentation theory approach we adopt, again despite the same physical basis for the models. In [21], the authors are motivated by the idea of a large fluctuating capture zone being constrained by its neighbours, rather than any attempt to consider in detail how the nucleation process impacts on the large size CZD behaviour. In this work we have been able to prove that for $i = 0$, the large size dependence of the CZD following equation (4) mirrors that of the corresponding gap distribution $\phi(y)$. In particular, we have $P(s) \sim \exp(-2s^3/\mu^3)$ rather than the Gaussian tail of equation (1). Furthermore, whilst it remains unproved, we can conjecture that the CZD for larger values of i will similarly follow the asymptotics of the corresponding GSD and follow $\exp(-c_i s^{2i+3})$ for some constants c_i in stark contrast to the Gaussian tail.

In conclusion, we have shown that the GWS of [21] is in conflict with the asymptotic solutions to the fragmentation theory analysis of point island nucleation and growth in one dimension. Given that the physical basis of the two approaches is the same, we believe that these differences show important failings of the GWS. Of course, this is not to claim that the Blackman and Mulheran model, embodied in equations (3) and (4) above, has been proven to be correct; confrontation with simulation and experiment will ultimately arbitrate between these theories. Along these lines, we note the recent analysis of the case of $i = 1$ in [13], and our own detailed comparisons with extensive simulation data for $i = 0, 1, 2, 3$ presented in [20].

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